



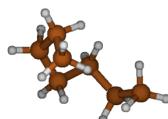
Predicting Unimolecular Kinetics and Dynamics in the Low Pressure Limit

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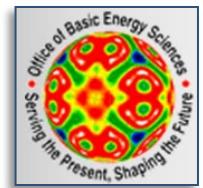
Co-workers

**Marco Verdicchio, Kenley Pelzer, Jim Miller,
Larry Harding, and Stephen Klippenstein, Argonne**



Jeff Steill and Dave Chandler, CRF, Sandia

\$US
DOE
BES



The origin of pressure dependence

Lindemann, Hinshelwood, O. K. Rice & Ramsperger, ... 1920s



In the high pressure limit (k_∞)

$$k_{\text{TST}} \ll k_{\text{collisions}}$$

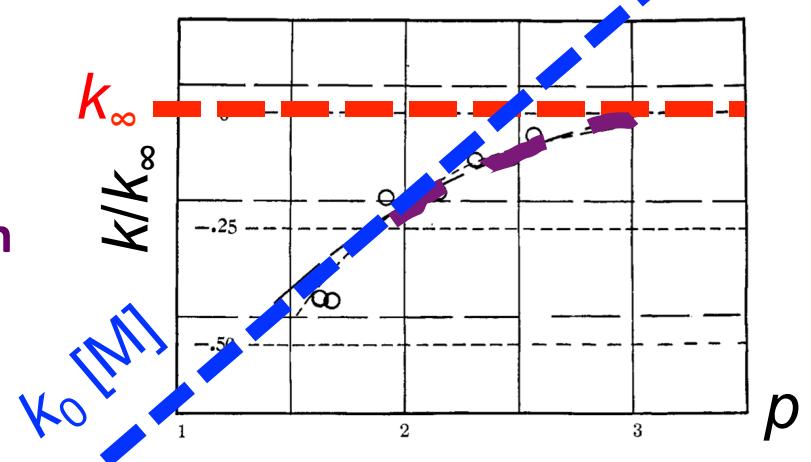
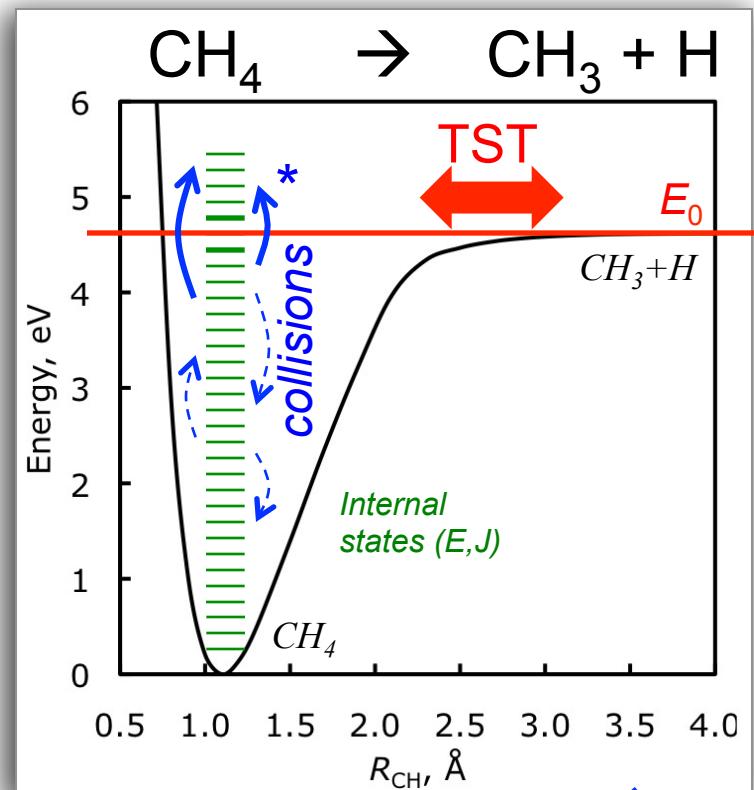
The TS is rate limiting

In the low pressure limit ($k \propto k_0 p$)

$$k_{\text{TST}} \gg k_{\text{collisions}}$$

Activating collisions are rate limiting

Competition modeled via a master equation





Microcanonical unimolecular rate coefficients



The “state” (E,J) collects nearby quantum states with ($E+\delta E, J+\delta J$)

$$k_p(T) = \sum_{J=0}^{\infty} \int_0^{\infty} dE \kappa_p(E, J) x_p(E, J)$$

↑
microcanonical rate coefficients

reactant populations

HPL: x_{∞} = Boltzmann/thermal ($= \rho \exp(-E/k_B T)/Q$)
 κ_{∞} = TST/“RRKM” ($= N^{\ddagger}/h\rho$)

LPL: x_0 = Steady state populations

Solve ME: ~thermal but depleted near threshold

κ_0 = Reactive collisional energy transfer rate
= $Z \times F(E, J)$

A + M collision rate X fraction of activating collisions



Microcanonical unimolecular rate coefficients

Low-pressure limit kinetics



4D $Z P(E, J; E', J')$ = state-to-state collisional transfer rate coef.

Sum over
reactive final
states

$$F(E', J') = \sum_{J=0}^{\infty} \int_{E_J}^{\infty} dE P(E, J; E', J')$$

Microscopic detail

2D $\kappa_0 = Z F(E', J')$ = microcanonical rate coefficient

Sum over all
initial states

$$k_0(T) = Z \sum_{J'=0}^{\infty} \int_0^{\infty} dE' F(E', J') x_0(E', J')$$

0D κ_0 = thermal rate coefficient

$P(E,J;E',J')$ has been well studied with trajectories

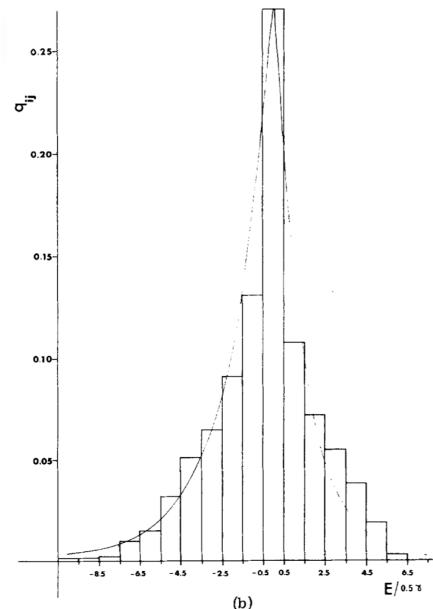
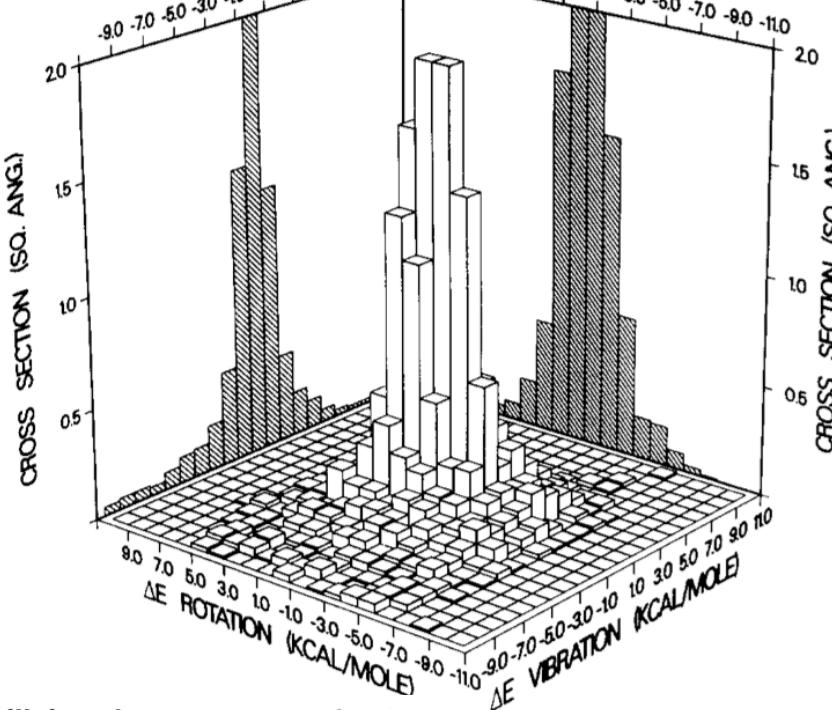


FIG. 5. As for Fig. 4. (a) O₃/Ar at 500K ($\gamma = 0.0199$ eV, $b_{\max} = 8.0 \alpha_0$, (b) O₃/Ar at 2500K ($\gamma = 0.0861$ eV, $b_{\max} = 8.0 \alpha_0$).



A classical trajectory study of collisional energy transfer in thermal unimolecular reactions

A. J. Stace ^{a)} and J. N. Murrell

JCP 1978

Collisional energy transfer in the low-pressure-limit unimolecular dissociation of HO₂

Nancy J. Brown
Applied Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

James A. Miller
Combustion Chemistry Division, Sandia National Laboratories, Livermore, California 94550

JCP 1984

Many studies since

Oref
Gilbert
Schatz
Lendvay
Lim
Hase

Recent work

Barker & Weston

Thompson &
Wagner

Bowman & Houston

Motivation

Much is known about $P(E,J;E',J')$

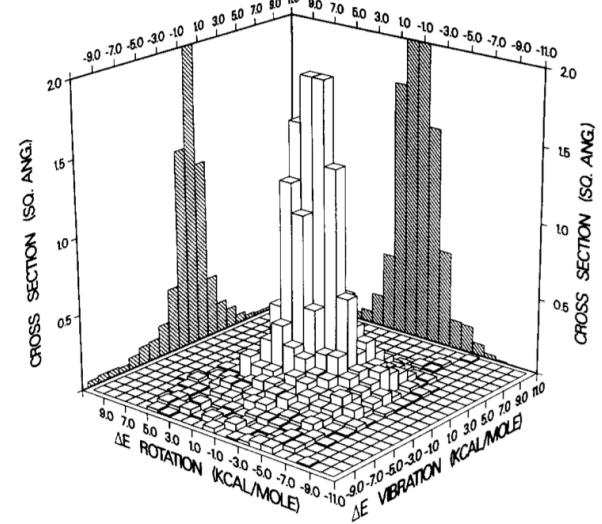
- But this information has not made its way into kinetics calculations

We wish to understand

- Which details of CET are important kinetically?
- How accurately can we calculate these details?
- How can we incorporate the important details into complex kinetics (master equation) calculations?
- How accurately can we predict LPL kinetics?

Methods

- Ab initio-based PESs
- Classical trajectories for predicting
 Z = Collision rates
 $F/P = \Delta E$ and ΔJ transfer probabilities



*Can we avoid
characterizing P in
so much detail?*



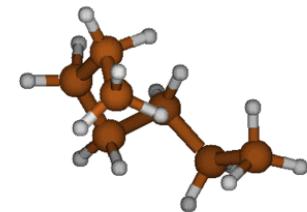
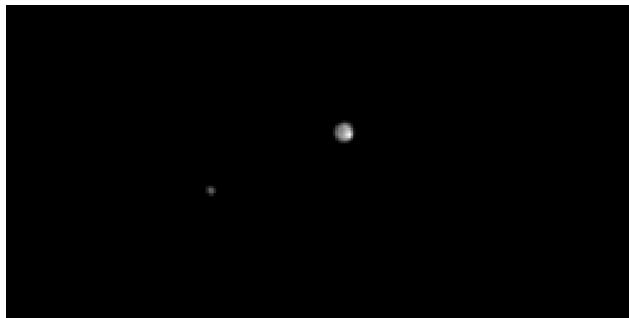
Here we predict Z and F using full-dimensional PESs and classical mechanics

Classical mechanics can be accurate for molecular systems

- + LPL kinetics most sensitive to $E \approx E_{\text{threshold}}$
- + We are predicting highly-averaged energy/angular momentum transfer, not fine details
- + Straightforward initial conditions/final state analyses for
$$A(E',J') + M \rightarrow A^*(E,J) + M$$
- + Reaction need not be explicitly modeled in the LPL (no $A^* \rightarrow B$)

We can use quantized thresholds for reaction

Simplifies PES construction



Ar + heptane at 1000 K

Pluto & Charon (New Horizons, April)



PESs for collisional energy transfer

In general,

$$V = V_A + V_M + V_I$$

CET most sensitive
to this term

V_I : We use both analytic/fitted PESs and direct dynamics

(a) Separable/pairwise approximation for atomic/diatomic M

e.g., $V_I = \sum_i A_i \exp(-R_i/B_i) - C_i/R_i^6$ i = intermol. atom-atom distances

parameterized against counterpoise corrected CCSD(T)/CBS cuts

(b) Separable/non-pairwise for very isotropic A + M (e.g., HO₂ + N₂)

e.g., $V_I = \sum_a c_a P[\prod_i y_i^{n_{ia}}]$ a = basis funcs.; $y_i = \exp(-R_i)$; P = symmetrizer

parameterized against counterpoise corrected CCSD(T)/CBS grids

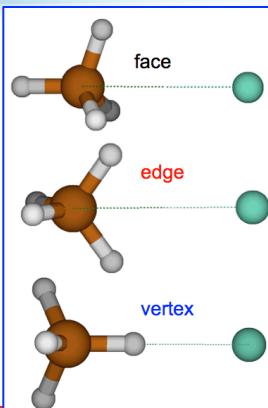
(c) Non-separable/non-pairwise direct dynamics for small systems

Choose the empirically best MP2(SAC)/~dz method compared to CCSD(T)/CBS

~SRP : Optimize SAC scaling parameter & basis set (Gordon/Truhlar)

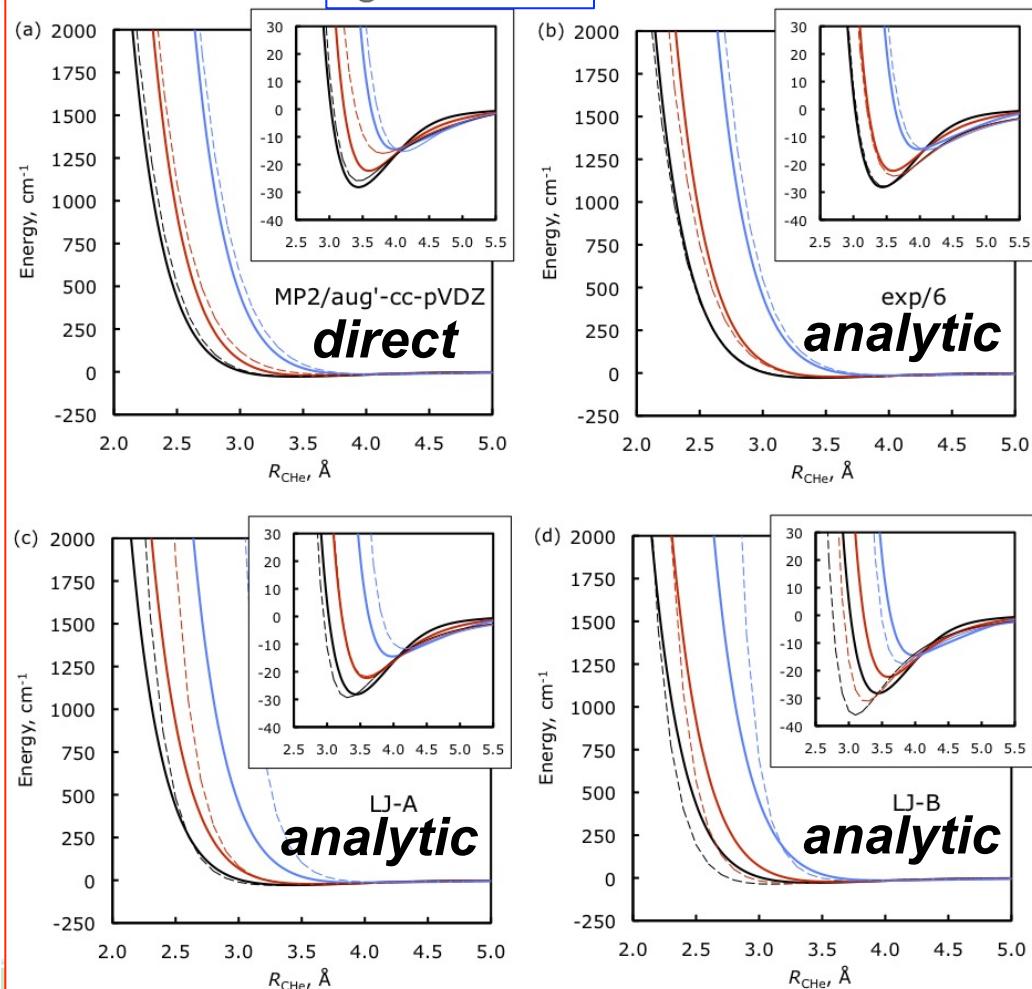
$$E_{\text{SAC}} = E_{\text{HF}} + f_{\text{SAC}} (E_{\text{MP2}} - E_{\text{HF}})$$

Solid =
CCSD(T)/CBS

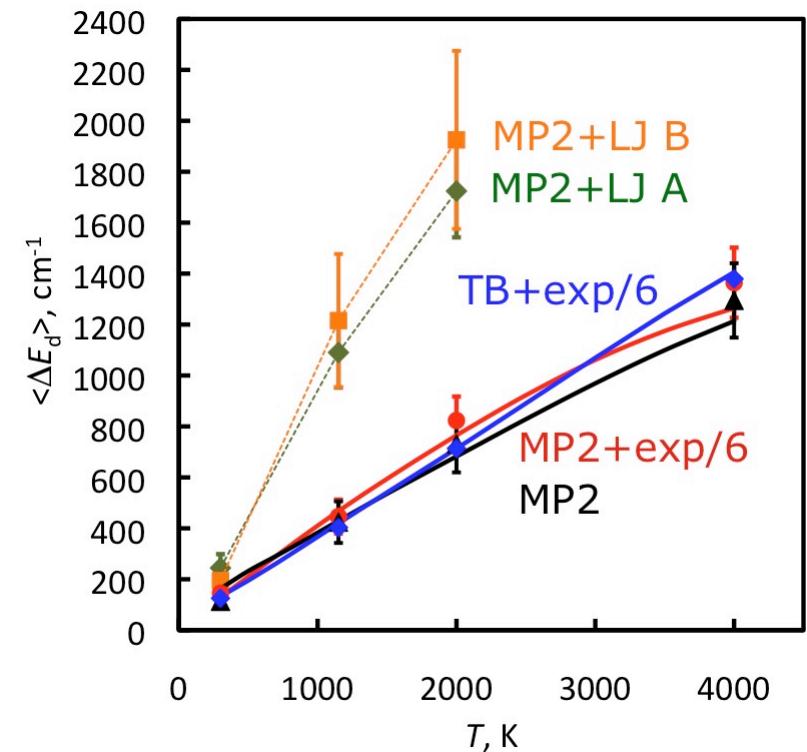


Test of the separable approximation vs direct dynamics

$\text{CH}_4 + \text{He}$



Avg ΔE in deactivating collisions



CET is

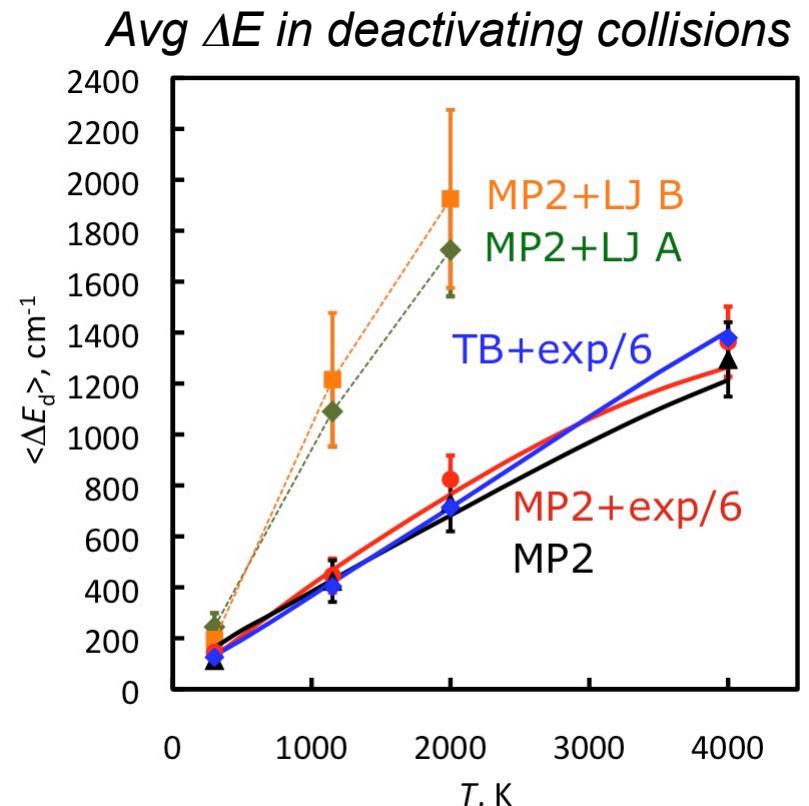
- very sensitive to the repulsive wall
- insensitive to the internal PES
- “separable” approximation for weak interactions is OK

Test of the separable approximation vs direct dynamics

Table 3. Frequencies ω and Rotational Constants B for CH₄ (cm⁻¹)

	ω				B
experimental ^a	3019	2917	1534	1306	5.24
MP2 ^b	3209	3065	1565	1344	5.19
SAC ^b	3194	3042	1545	1321	5.19
TB	3252	3162	1690	1570	5.24

^a Ref 30. ^b The aug'-cc-pVDZ basis set was used for the MP2 and SAC calculations.

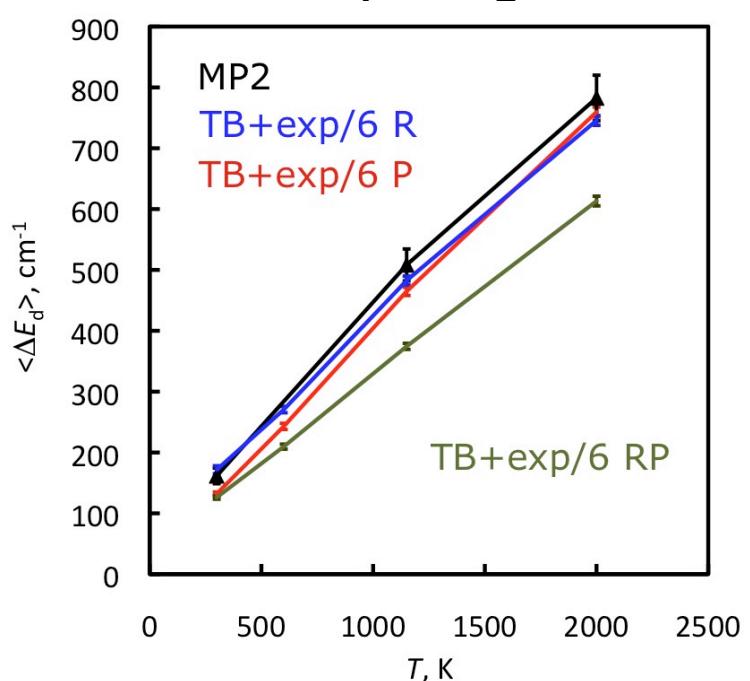
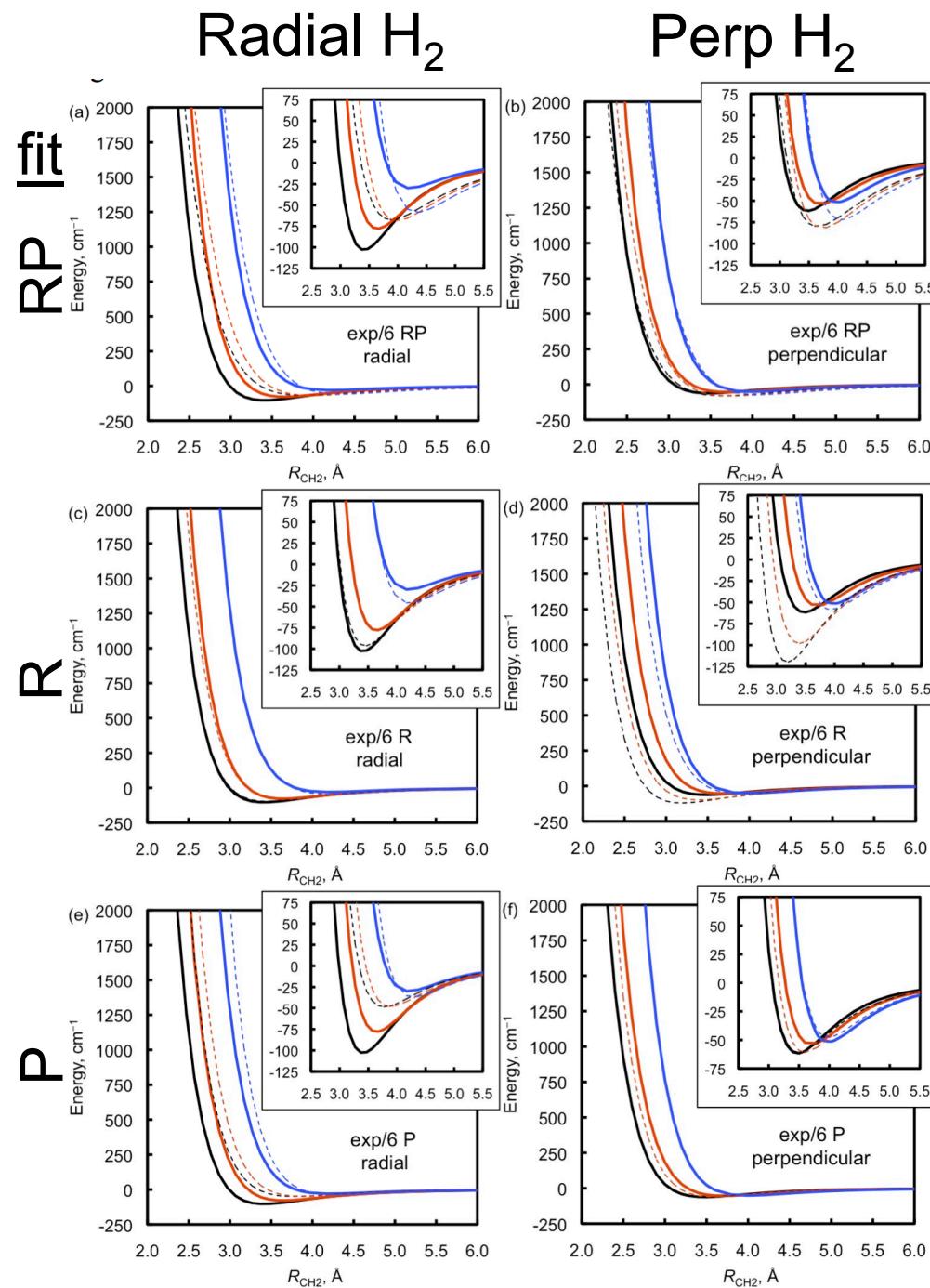


Insensitivity to the internal PES

- SAC vs TB, $\rho(E_{\text{thresh}}, J=0)$ differs by 40%
- ρ enters into $P(E, J; E', J')$ via detailed balance

$$P \propto \left[\frac{\rho(E, J)}{\rho(E', J')} \exp\left(\frac{-|\Delta E|}{k_B T}\right) \right]^{\frac{1}{2}}$$

Tests of the separable approximation vs direct dynamics



Pairwise fails for this simple system
But CET moments differ by only 25%
Simple PESs can be accurate
“Validated” PESs are even better
Errors due to the PES < 25%

Predicting collision rates Z from full-D PESs

Observable = $\Delta E / \text{collision} \times \text{collisions} / \text{time}$

Practical approach

Use effective one-dimensional models

12/6 LJ form is OK for most systems, exp/6 can be used

Need two LJ parameters ϵ and σ

Bad: Orientation-average then minimize (>40% errors in Z)

R_{com} vs. $\langle V \rangle$

Good: Minimize then orientation-average (<10% errors in Z)

V vs. $\langle R_{\text{com}} \rangle$

~70 comparisons w/ tabulated
(w/ Jim Miller C&F 2014)

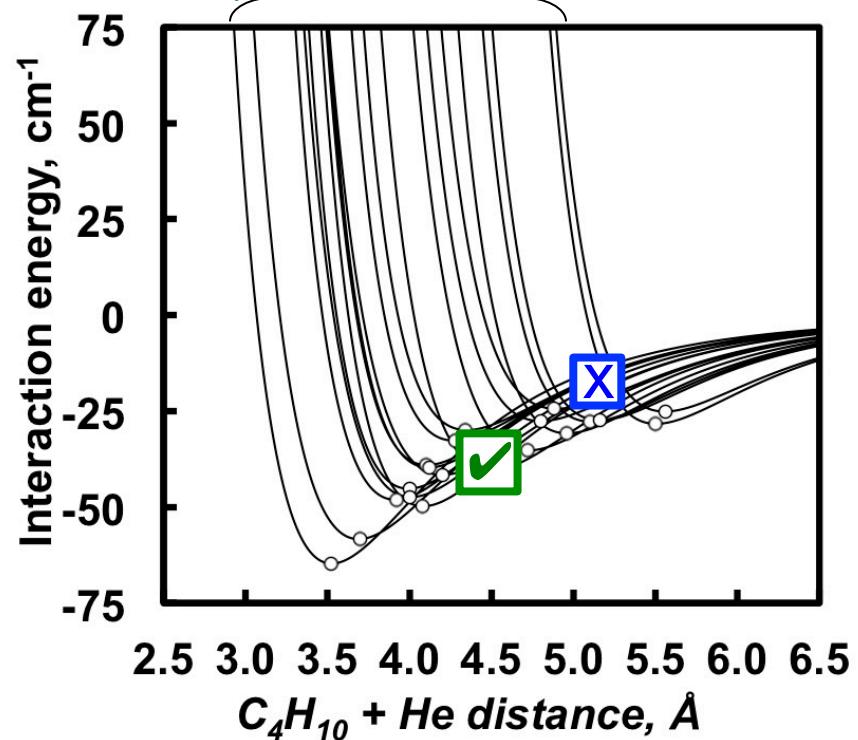
Simple trends for $C_xH_y + M$ relative to $CH_4 + M$

$$\sigma = \sigma_{CH_4+M} x^{0.15}$$

$$\epsilon = \epsilon_{CH_4+M} x^{0.25-0.40}$$

*predicts 266 calculated
binary 12/6 LJ collision
rates to better than 5%*

**butane + He cuts through
the interaction potential for
20 random orientations**



Predicting collision rates Z from full-D PESs

“Exact” classical collision rates

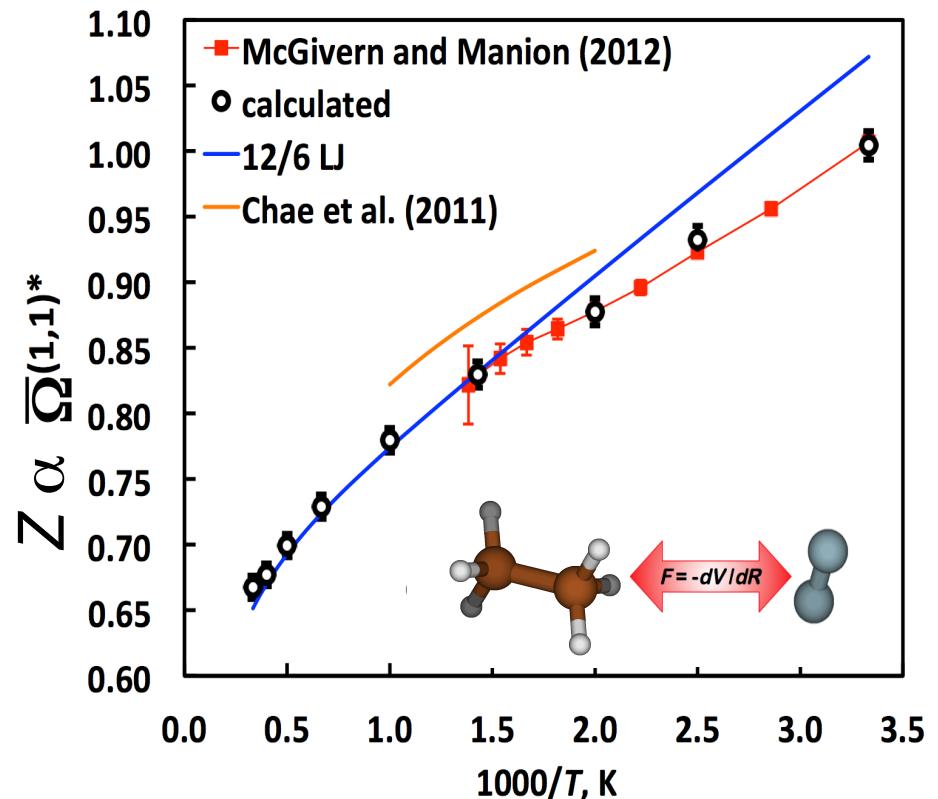
Z (and transport properties) are functions of collision integrals

$$\Omega^{(1,1)*}(T) = \frac{1}{\pi\sigma^2} \sum_{i,j,i',j'} \frac{e^{-\varepsilon_{A,i}}}{Q_A} \frac{e^{-\varepsilon_{B,j}}}{Q_B} \int d\gamma \gamma^3 e^{-\gamma^2} \times \int d\phi \sin \chi d\chi (\gamma^2 - \gamma \gamma' \cos \chi) I_{ij}^{i'j'}$$

Collisionally-averaged deflection angle χ

We recast $\Omega^{(1,1)*}$ as a Monte Carlo integration over classical collisions

$$\Omega^{(1,1)*}(T) = \frac{b_{\max}}{\sigma^2} \sum_{\alpha} b_{\alpha} (\varepsilon_{\alpha} - \sqrt{\varepsilon_{\alpha} \varepsilon'_{\alpha}} \cos \chi_{\alpha}) / N$$



Separable pairwise analytic PES

W. S. McGivern and J. A. Manion, *Combust. Flame* **159**, 3021 (2012).

K. Chae, P. Elvati, and A. Violi, *J. Phys. Chem. B* **115**, 500 (2011).



Predicting $F(E',J') = \kappa_0(E',J')/Z$ via trajectories

(1) Calculate directly via trajectories

- Initial internal state of A(E',J') sampled microcanonically
- Initial internal state of M sampled thermally at temperature T
- Relative A + M sampled via usual bimolecular thermal rules at T
- Count “reactive” trajectories using quantized rotationally adiabatic thresholds

A* is reactive if $E > E_J$

$$F(E',J') = \kappa_0(E',J')/Z = \frac{Z_{\text{HS}}(b_{\max})}{Z} \sum_i \Theta(E^{(i)} - E_{J^{(i)}})/N$$



Predicting $F(E',J')$ via models

(2) Via detailed models for $P(E,J;E',J')$

The most detailed model considered here is similar to Barker and Weston's.

Ours has 9 parameters

$$P \propto \exp[-(\Delta\bar{E} / \alpha(J'))^{\chi_\alpha}] \exp[-(\Delta\bar{J} / \gamma(J'))^{\chi_\gamma}]$$

$$\Delta\bar{E} = |\Delta E \cos\theta(J') - \Delta J \sin\theta(J')| \quad \alpha = \alpha_0 + \alpha_1 J'$$

$$\Delta\bar{J} = |\Delta E \sin\theta(J') + \Delta J \cos\theta(J')| \quad \gamma = \gamma_0 + \gamma_1 J'$$

Features

- (1) ~exp in both ΔE and ΔJ
- (2) Stretched via χ
- (3) Non-separability via θ
- (4) J' dependence

Other models that have been used in kinetics calculations

$P \propto \exp[-(\Delta E / \alpha)]$ **Single exponential down:** $\alpha = \langle \Delta E_d \rangle$, J, J' are neglected

$P \propto \exp[-(\Delta E / \alpha)]\varphi(J)$ **Statistical collider in J :** final J independent of initial state & assumed statistical

$P \propto \exp[-(\Delta E / \alpha)] \exp[-(\Delta J / \gamma)]$ **Weak collider in J :** J -dependence, $\gamma = \langle \Delta J_d \rangle$

Note: Detailed balance and normalization enforced using **Barker & Weston's** prefactor g along with the strategy of **Jeffrey, Gates & Smith**

$$P(E, J; E', J') = C(E', J')^{-1} \hat{g}(E, J; E', J') \Pi(E, J; E', J')$$

Parameterizing the detailed model for P

$$P \propto \exp[-(\Delta\bar{E} / \alpha(J'))^{\chi_\alpha}] \exp[-(\Delta\bar{J} / \gamma(J'))^{\chi_\gamma}]$$

$$\Delta\bar{E} = |\Delta E \cos \theta(J') - \Delta J \sin \theta(J')| \quad \alpha = \alpha_0 + \alpha_1 J'$$

$$\Delta\bar{J} = |\Delta E \sin \theta(J') + \Delta J \cos \theta(J')| \quad \gamma = \gamma_0 + \gamma_1 J'$$

$$\theta = \theta_0 + \theta_1 J'$$

Calculate several low-order moments of $(P \Delta E^m \Delta J^n)$:

$$\langle \Delta E^m \Delta J^n \rangle(E', J') = \int_0^\infty dJ \int_{-E_0}^\infty dE P(E, J; E', J') \Delta E^m \Delta J^n$$

“Double moments”: average over initial J' ; choose single initial energy E'

$$\langle \langle \Delta E_x^m \Delta J_y^n \rangle \rangle^{(l)} = \int_0^\infty dJ' g(J') J'^l \langle \Delta E_x^m \Delta J_y^n \rangle(E'_0, J')$$

135 moments through 3rd order: $m, n = 0-3$, $l = 0-2$, $x=up, down, total$

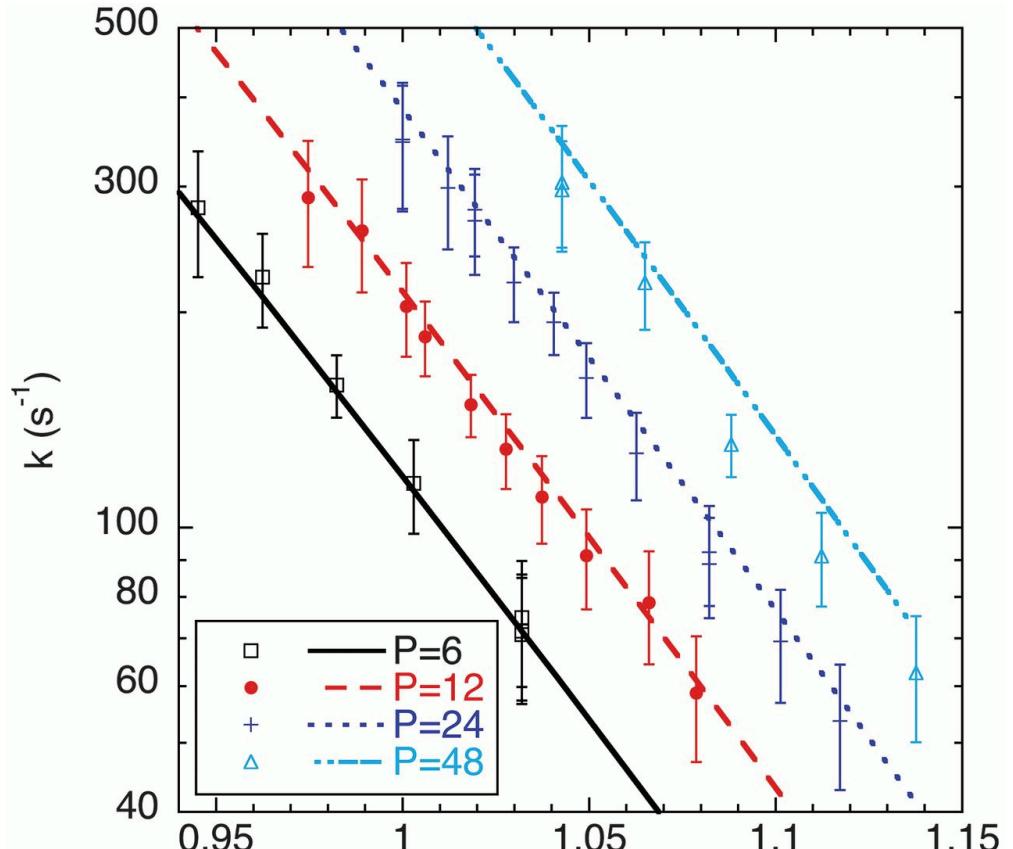
e.g., $m=1, n=0, l=0, x=down \rightarrow \langle \langle \Delta E_d \rangle \rangle^{(0)} = \langle \Delta E_d \rangle$

We fit the 9 parameters in P to reproduce the 135 trajectory-based moments.

Accuracy of the detailed model: Comparison of thermal rates with experiment



- Results in the low p limit
- Prediction most sensitive to P
- Solve master equation, which requires thermochemistry

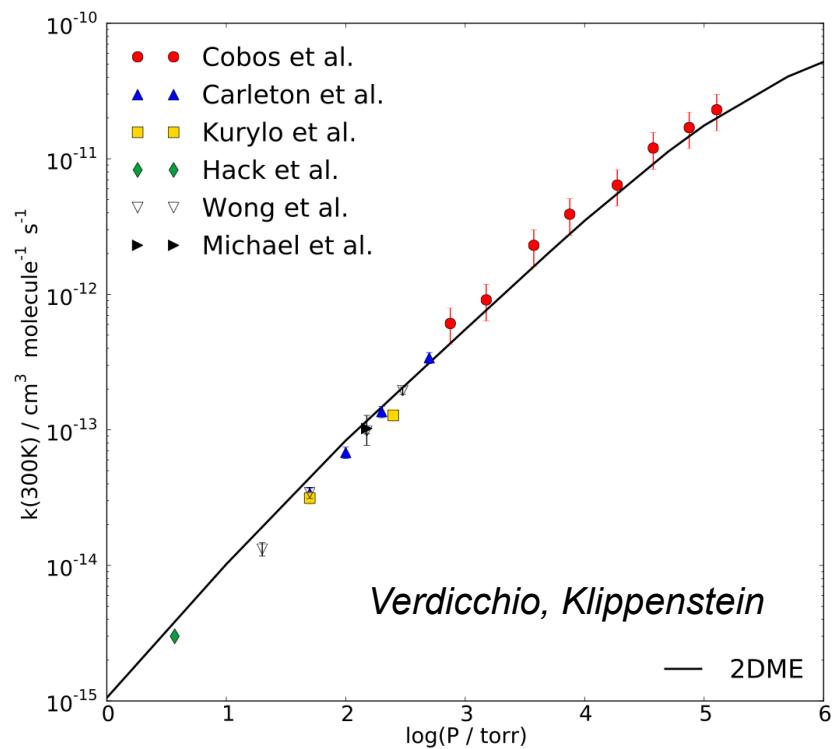
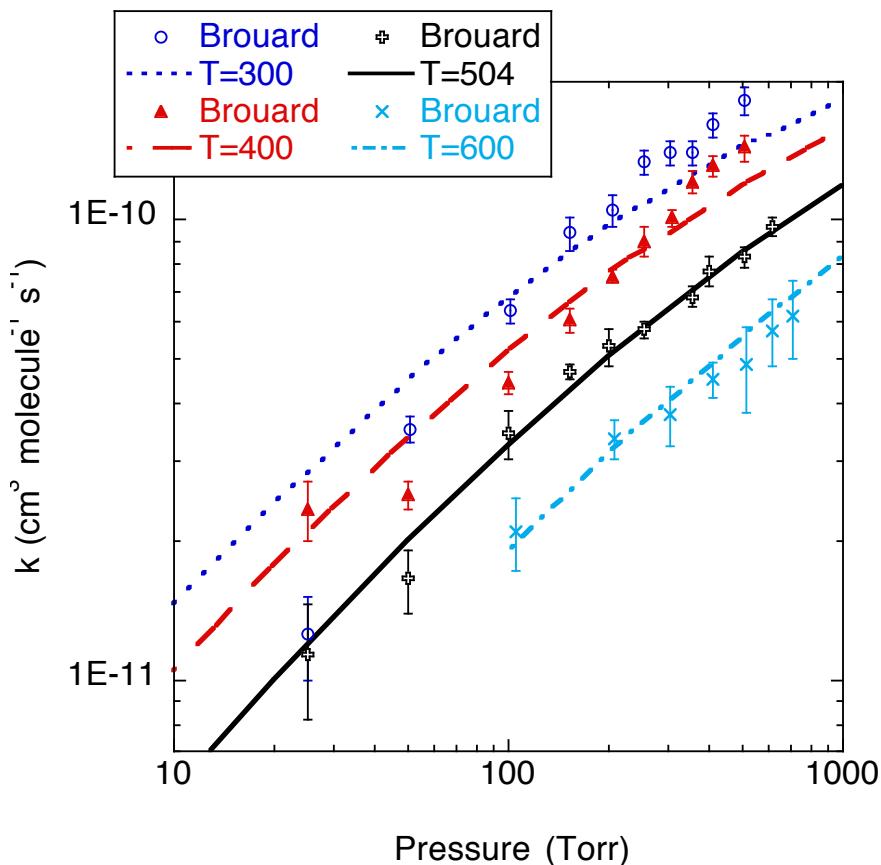


Symbols: Experimental results and error bars from Knyazev and Slagle, JPC 100, 16899 (1996).

Comparisons with experiments in the falloff

Solve master equation

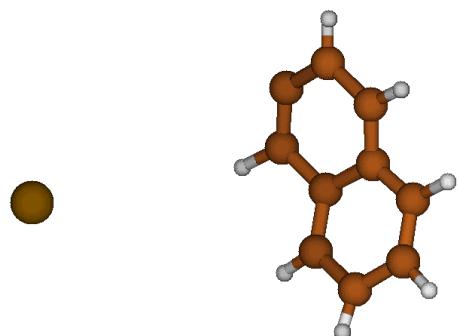
Results sensitive to thermochemistry HPL kinetics (VRC-TST, VTST)



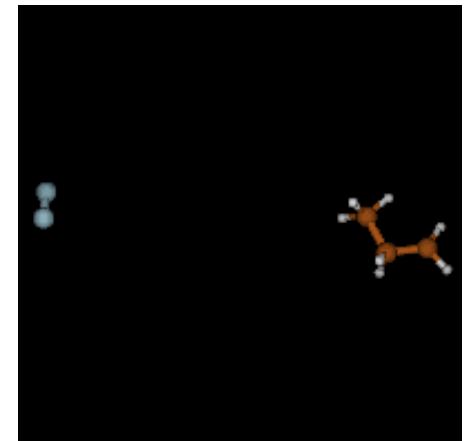
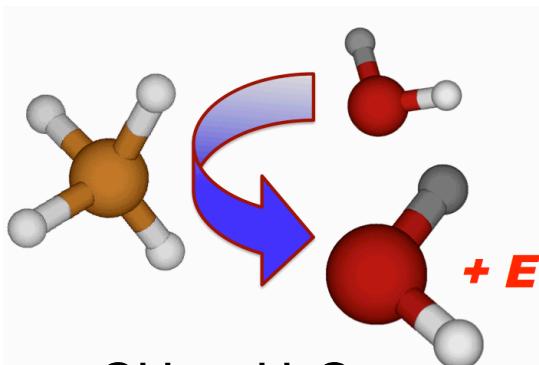
We have studied several different systems

A = molecules, radicals, triatomics ... PAHs

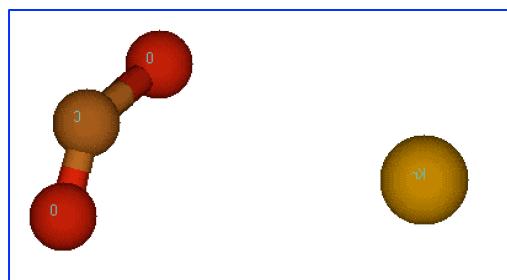
M = Rg, H₂, N₂, O₂, H₂O



1-naphthyl + Ar



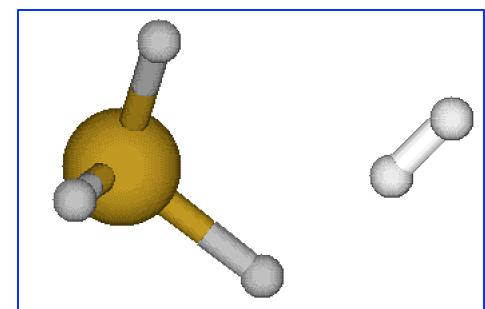
propyl + N₂



Spin-forbidden Kr + O + CO



CH₃OH + He



PH₃ + H₂



“First principles” error bars

Compute $k_0(T)$ for 3 different parameterizations

3rd: Full model, 9 parameters fit to 135 “double moments” through 3rd order

2nd: 9 parameters fit to 42 “double moments” through 2nd order:

$\langle\langle\Delta E^2\rangle\rangle, \langle\langle\Delta J^2\rangle\rangle, \langle\langle\Delta E\Delta J\rangle\rangle$, etc...

1st: 3 parameters fit to 6 1st order moments: $\langle\Delta E\rangle, \langle\Delta E_d\rangle, \langle\Delta E_u\rangle, \langle\Delta J\rangle, \langle\Delta J_d\rangle, \langle\Delta J_u\rangle$

Ratio of k_0 relative to 3rd order model for several systems, baths, temperatures

A + M	HO ₂ + Ar	HO ₂ + Ar	HO ₂ + He	HO ₂ + He	NAP + Ar	C ₂ H ₄ + Ar	CO ₂ + Kr	PH ₃ + H ₂	NH ₃ + H ₂	CH ₄ + H ₂	CH ₄ + N ₂	CH ₄ + He	CH ₄ + He	C ₂ H ₃ + He
T, K	300	1000	300	1000	1000	1000	1000	300	300	300	300	150	600	1000
2 nd /3 rd	1.00	0.88	0.88	0.97	0.69	0.97	1.15	1.00	1.08	1.26	0.75	0.79	0.97	0.97
1 st /3 rd	1.39	2.02	1.01	8.56	1.33	1.07	0.85	0.67	0.81	0.37	0.53	0.31	1.40	1.07
	avg	stdev			max		min							
2 nd /3 rd	0.96	0.15			1.26		0.69							
1 st /3 rd	1.53	2.08			8.56		0.31							

2nd order: 1σ error $\approx 15\%$
1st order: Not converged

Comparison with “model free” predictions

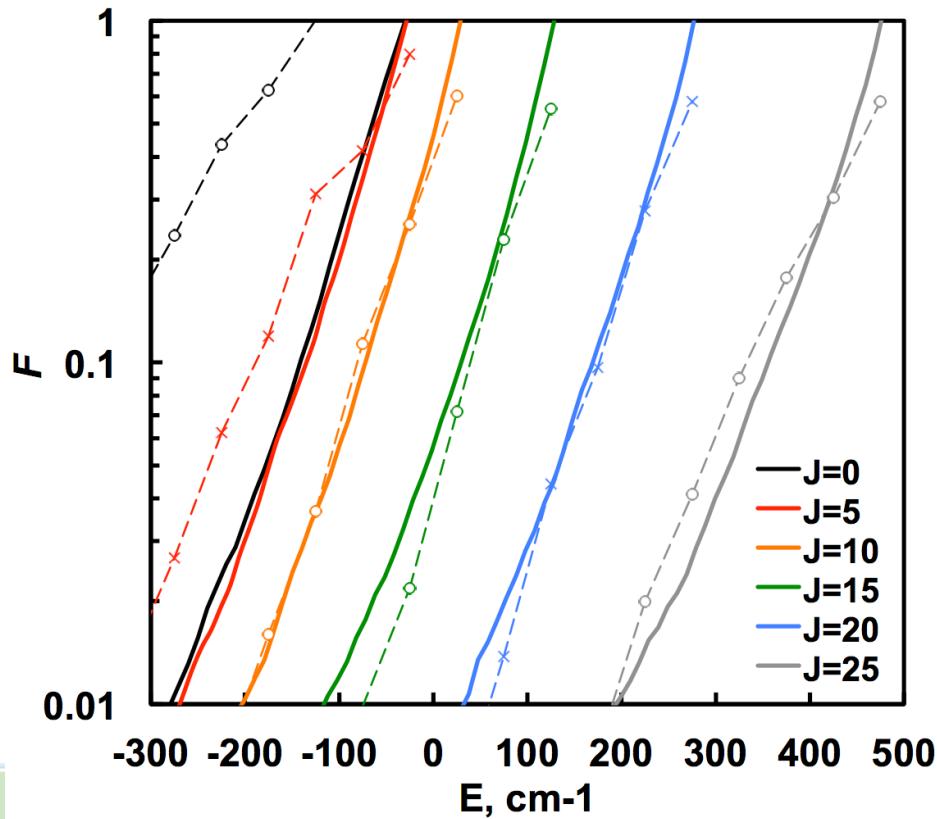
$\text{HO}_2 + \text{Ar}$ 300 K (Relevant $J = 5-25$)

Solid lines = “exact” classical results

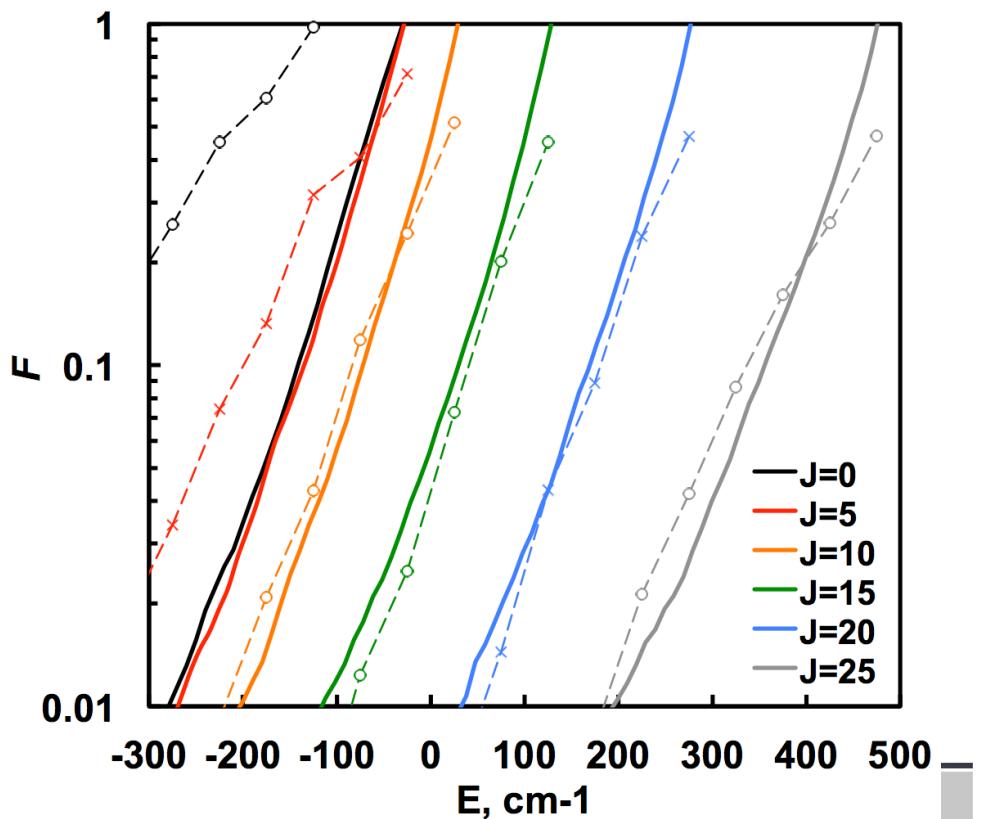
Dashed lines = master equation results for various models of P

	avg	stdev	max	min
2 nd /3 rd	0.96	0.15	1.26	0.69
1 st /3 rd	1.53	2.08	8.56	0.31

Full model for P , fit through 3rd order



Full model for P , fit through 2nd order



Comparison with “model free” predictions

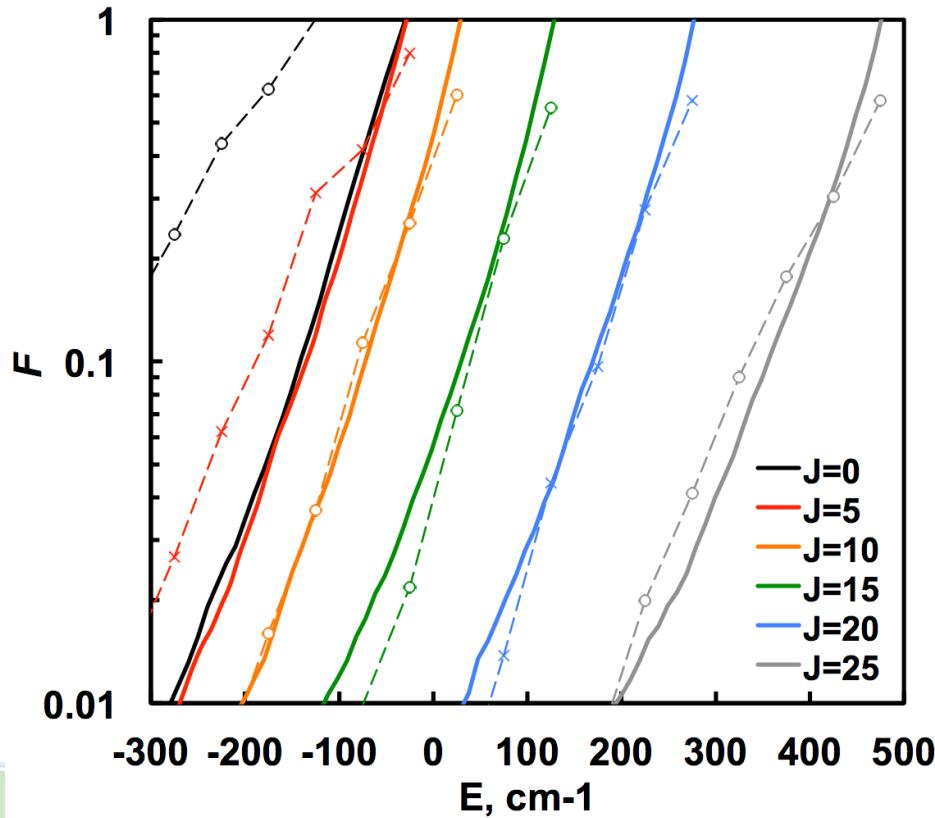
$\text{HO}_2 + \text{Ar}$ 300 K (Relevant $J = 5-25$)

Solid lines = “exact” classical results

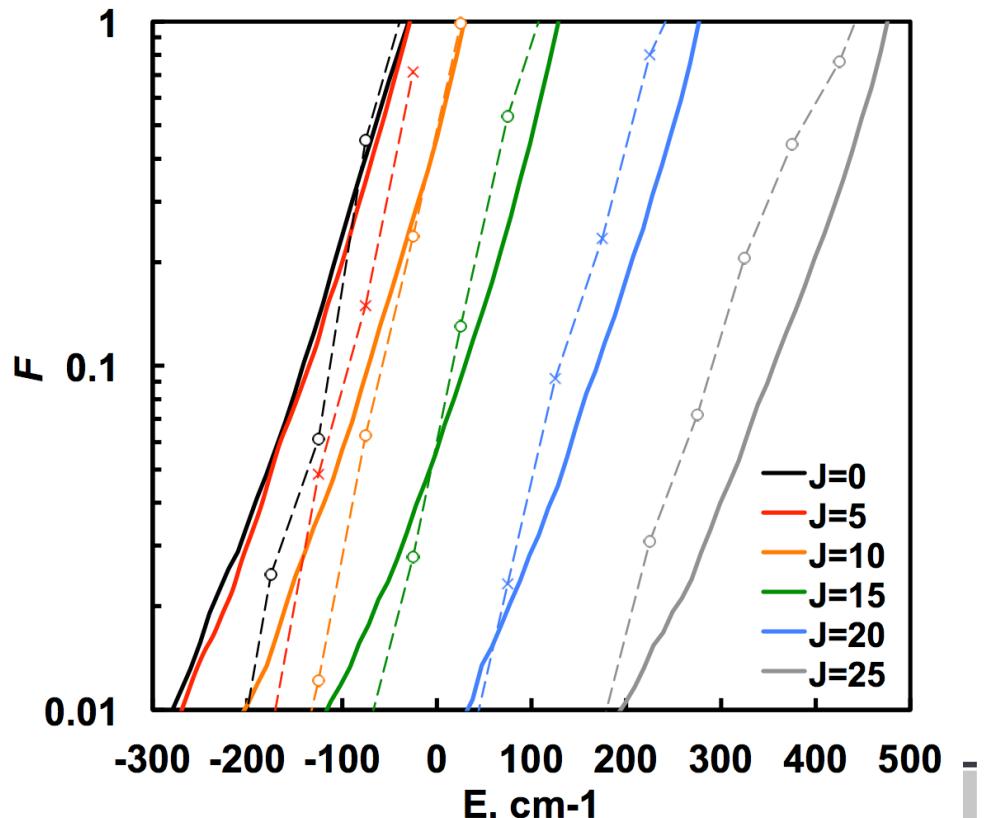
Dashed lines = master equation results for various models of P

	avg	stdev	max	min
2 nd /3 rd	0.96	0.15	1.26	0.69
1 st /3 rd	1.53	2.08	8.56	0.31

Full model for P , fit through 3rd order



Our model for P , fit through 1st order



Comparison with “model free” predictions

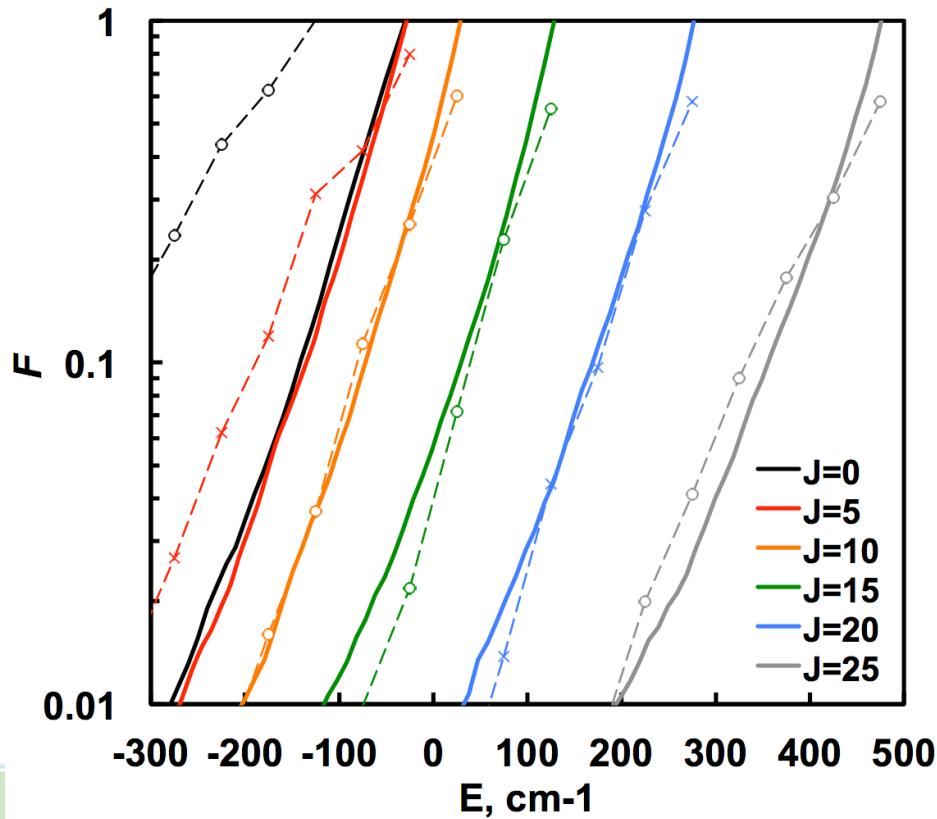
$\text{HO}_2 + \text{Ar}$ 300 K (Relevant $J = 5-25$)

Solid lines = “exact” classical results

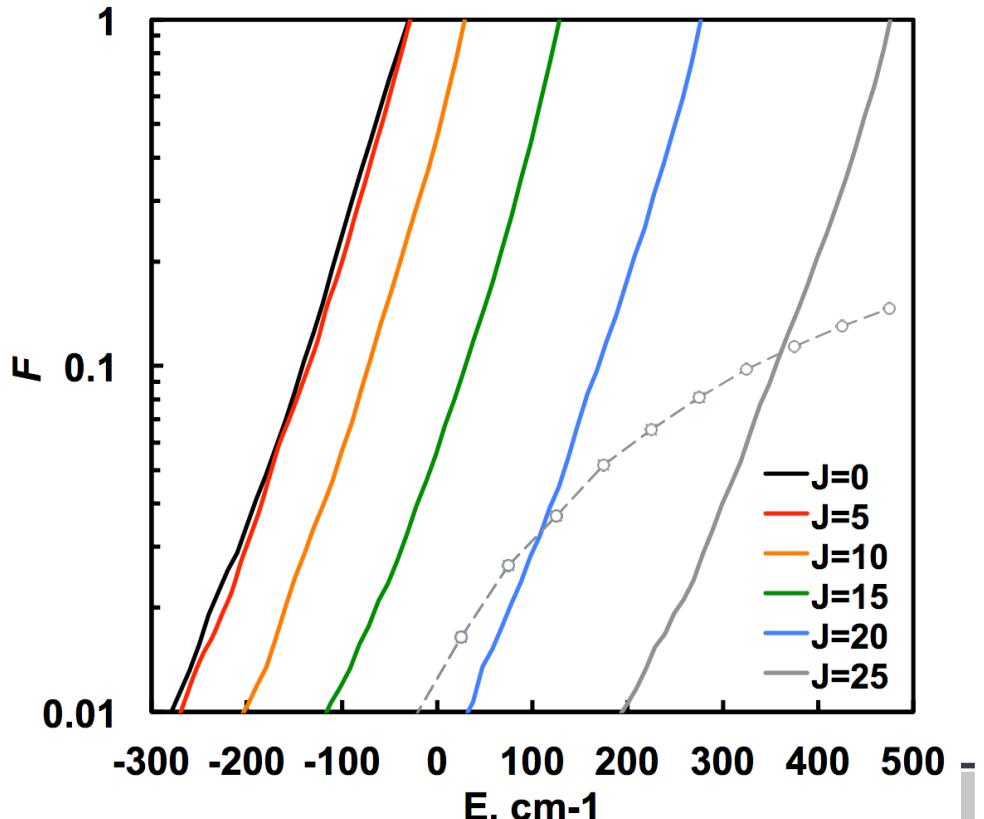
Dashed lines = master equation results for various models of P

	avg	stdev	max	min
2 nd /3 rd	0.96	0.15	1.26	0.69
1 st /3 rd	1.53	2.08	8.56	0.31
phi/3 rd	2.14	1.03	4.32	1.04

Full model for P , fit through 3rd order



Statistical strong collider in J model



Physics in *P*: Supercollisions

$$P \propto \exp[-(\Delta\bar{E} / \alpha(J'))^{\chi_\alpha}] \exp[-(\Delta\bar{J} / \gamma(J'))^{\chi_\gamma}]$$

$$\Delta\bar{E} = |\Delta E \cos\theta(J') - \Delta J \sin\theta(J')| \quad \alpha = \alpha_0 + \alpha_1 J'$$

$$\Delta\bar{J} = |\Delta E \sin\theta(J') + \Delta J \cos\theta(J')| \quad \gamma = \gamma_0 + \gamma_1 J'$$

$$\theta = \theta_0 + \theta_1 J'$$

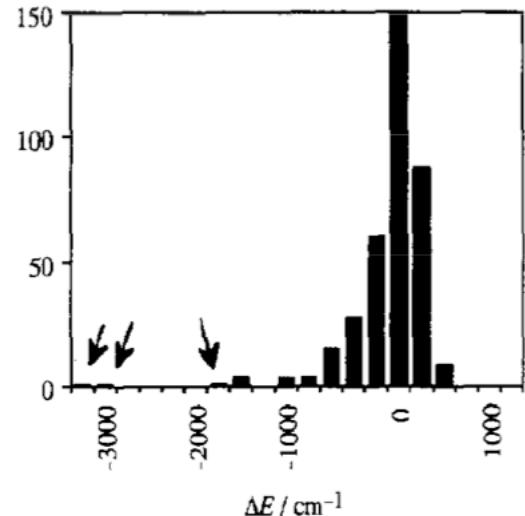
$\chi < 1$ stretches
the exponential

“Long tail” noted by Miller and Brown 1984

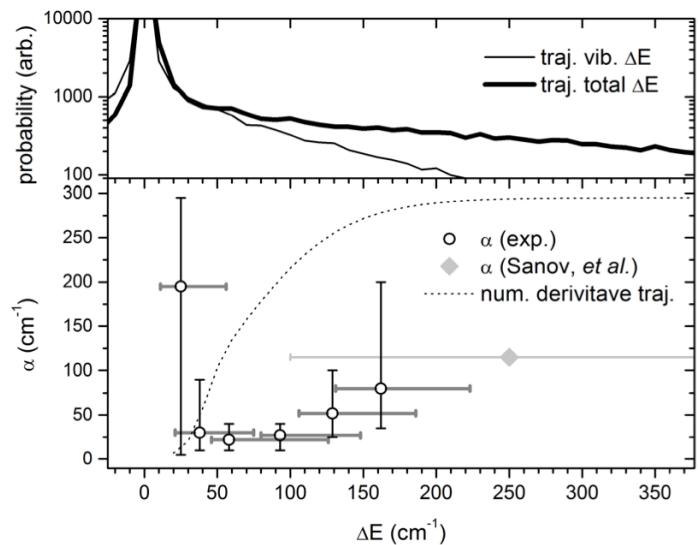
Supercollision events in weak collisional energy transfer
of highly excited species

David L. Clarke, Keiran C. Thompson and Robert G. Gilbert¹

CPL 1991

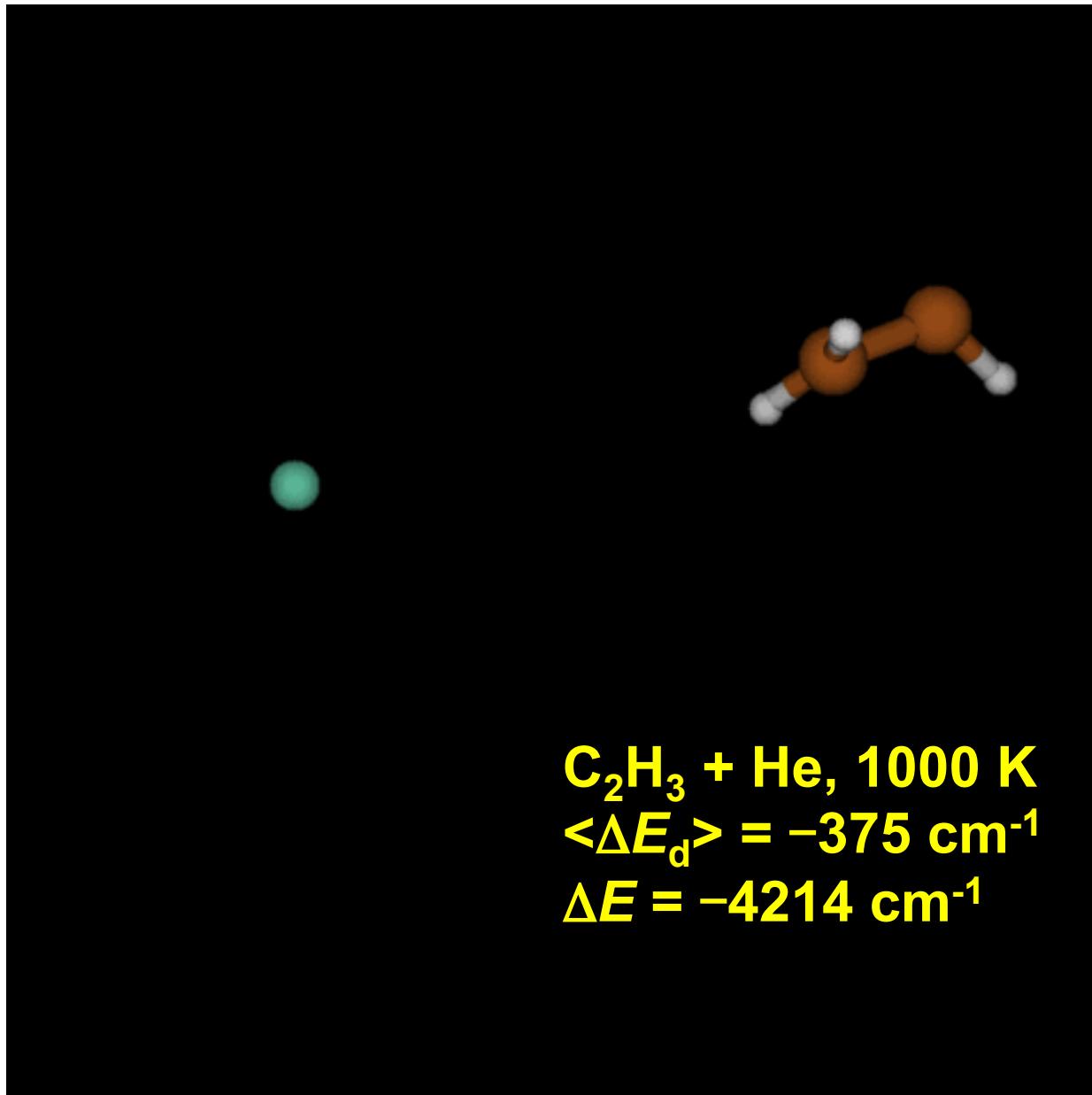


NO₂+Ar
Chandler's talk on Monday

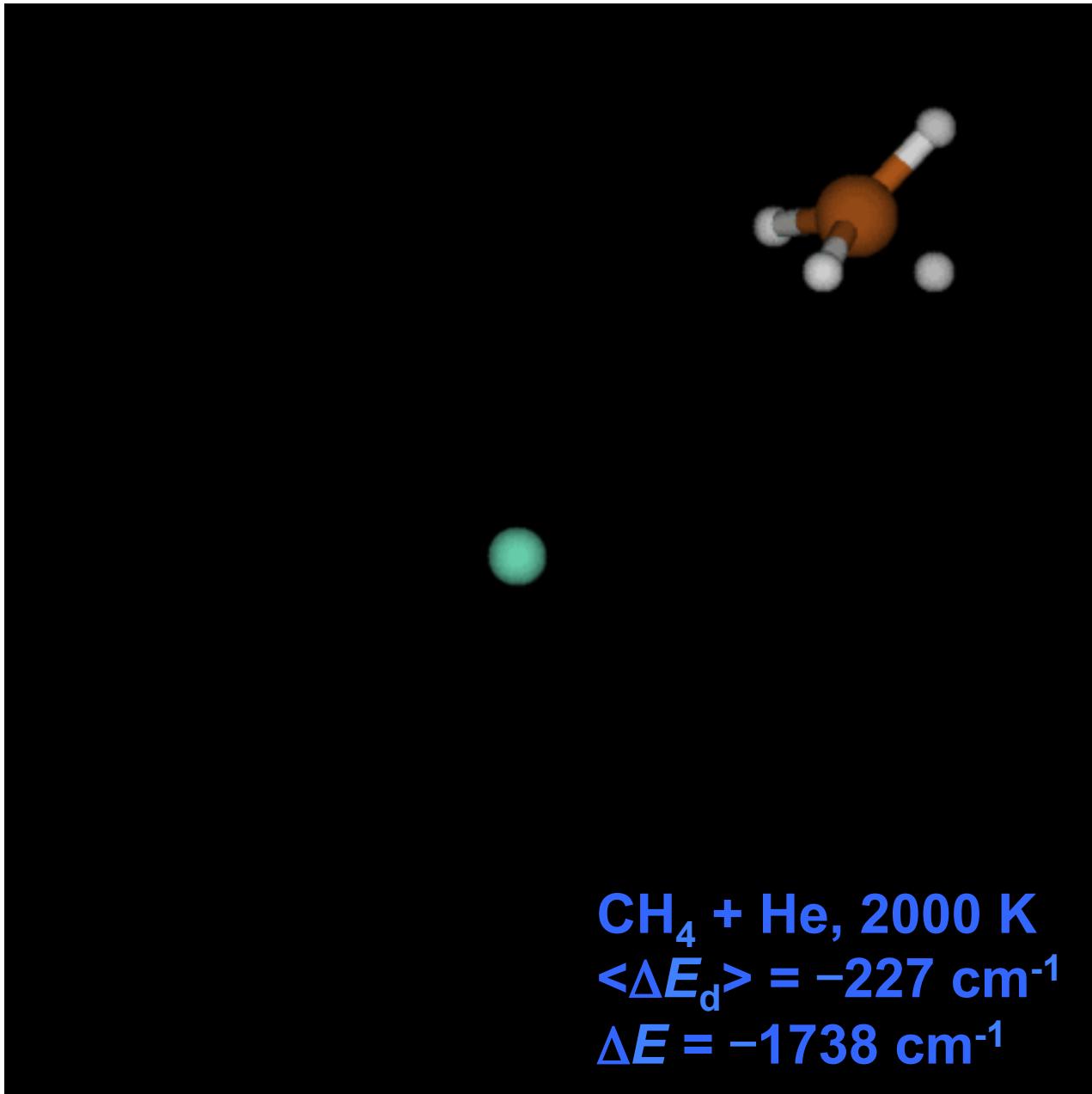


Steill et al.

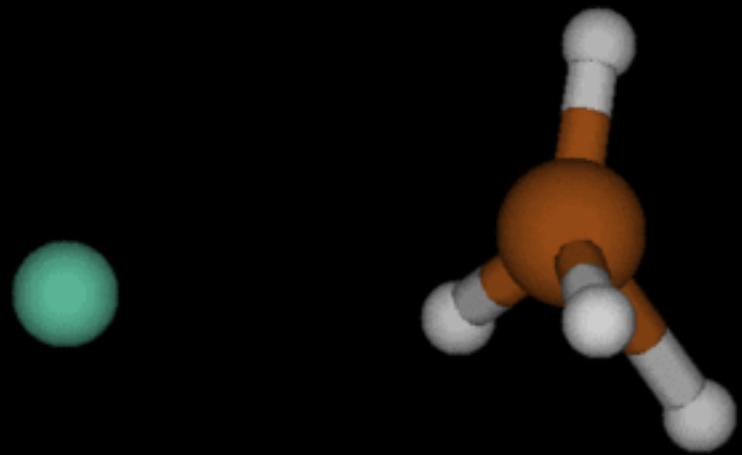
A supercollision of He + C₂H₃ via a wag



A supercollision of He + CH₄ via a stretch



Again



$\text{CH}_4 + \text{He}, 2000 \text{ K}$
 $\langle \Delta E_d \rangle = -227 \text{ cm}^{-1}$
 $\Delta E = -1738 \text{ cm}^{-1}$

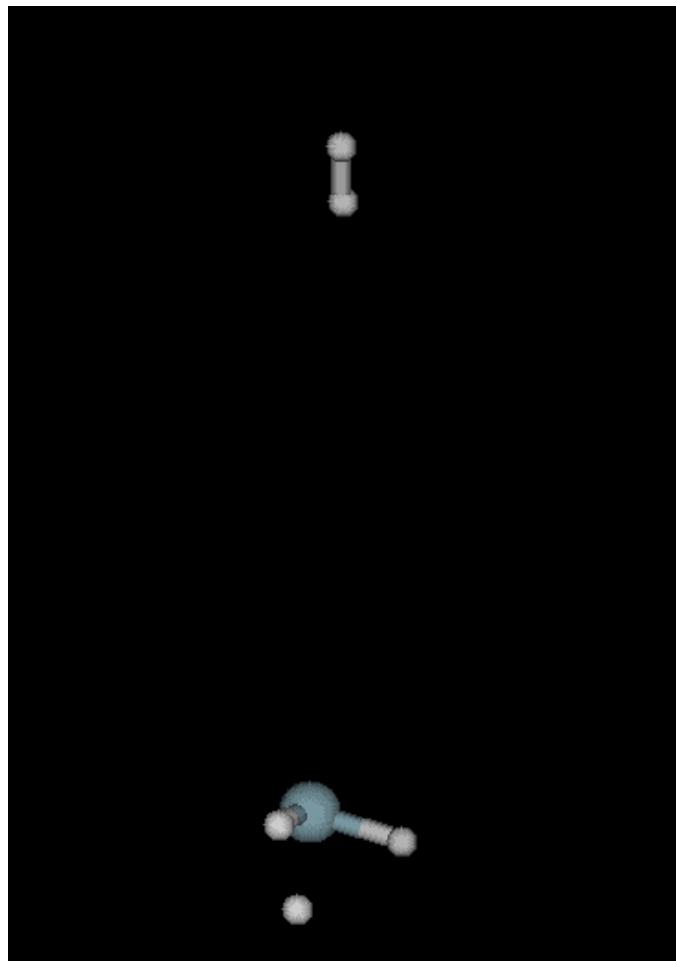
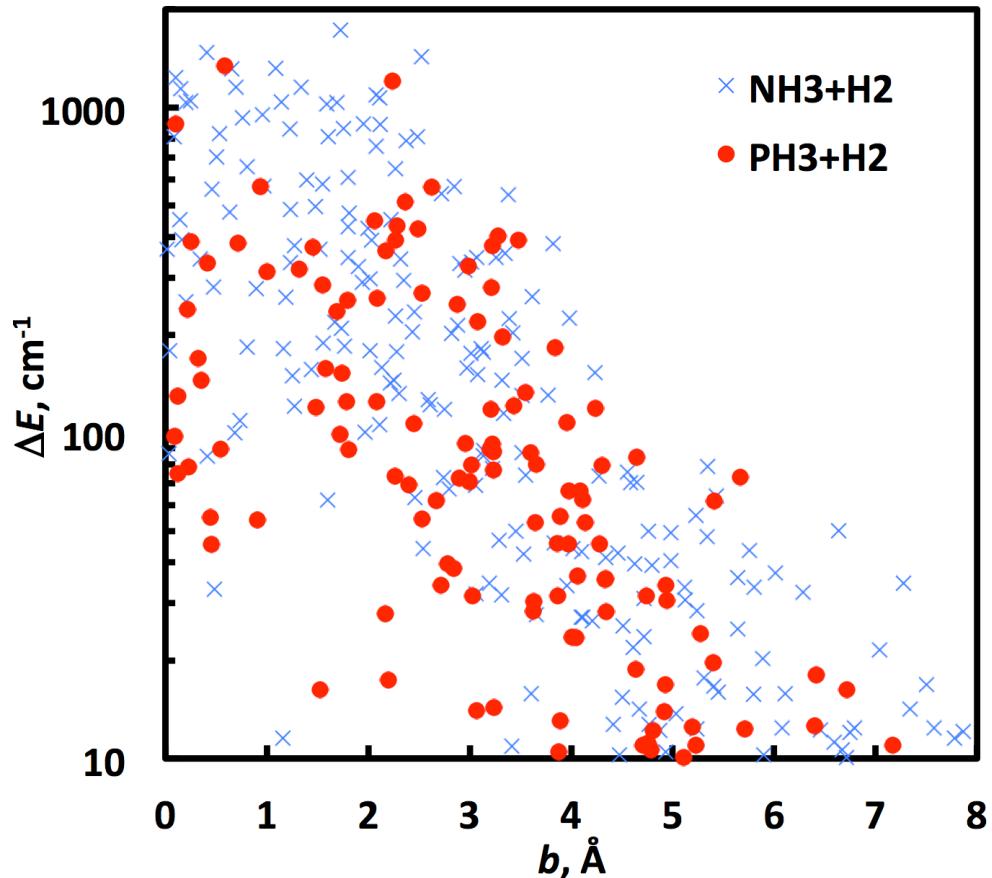
A supercollision in $\text{NH}_3 + \text{H}_2$ via an umbrella bend

$\langle \Delta E_d \rangle$ is $\sim 2x$ larger for $\text{NH}_3 + \text{H}_2$ than for $\text{PH}_3 + \text{H}_2$

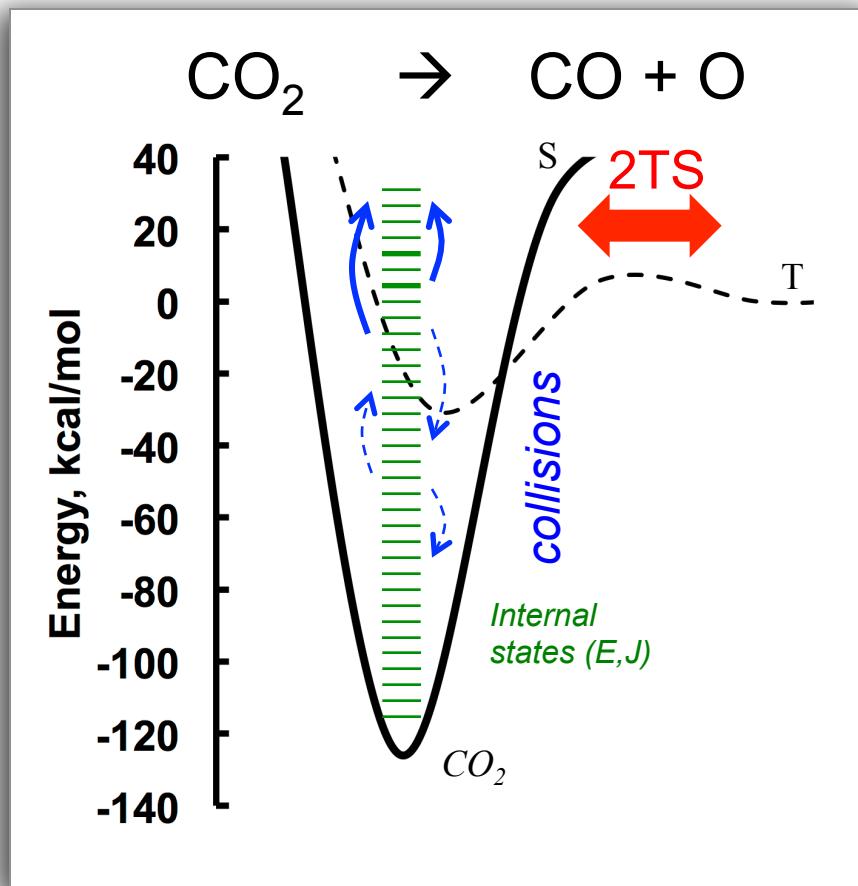
Dissociation energy (kcal/mol):

Inversion barrier (kcal/mol):

	NH_3	PH_3
Dissociation energy (kcal/mol):	106	78
Inversion barrier (kcal/mol):	6	32



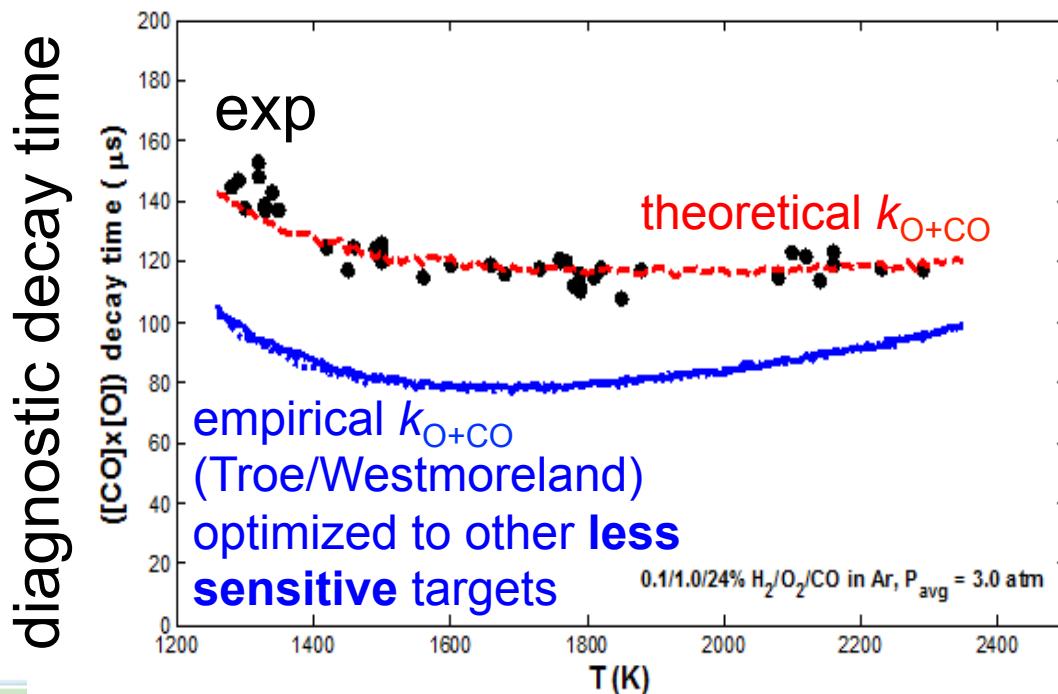
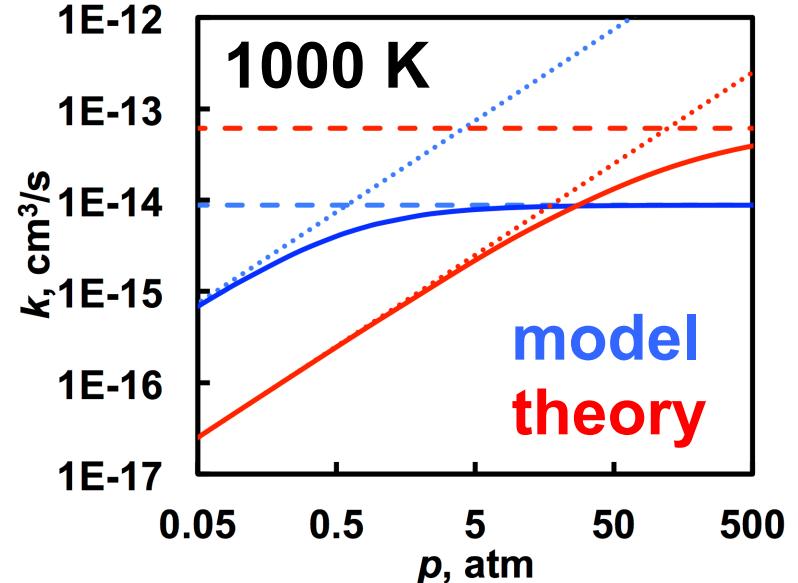
Combustion example: Spin-forbidden O + CO



Useful theoretical kinetics in practical combustion models

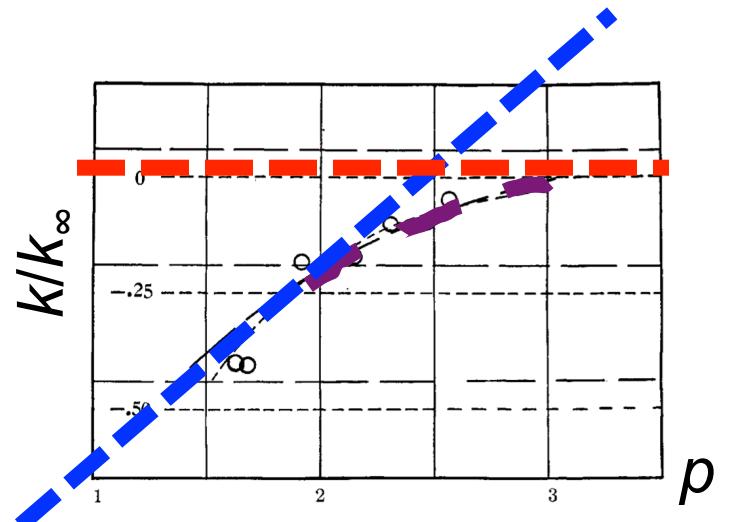
syngas H₂/CO combustion

- Haas, Dryer (Princeton) have a large detailed chemical kinetic mechanism
- Mac Haas identified modeling targets sensitive to k_{O+CO}



Conclusions

- The blue line can be calculated accurately using ab initio based PESs, classical trajectories, and a new model for P
- Low pressure limit kinetics is sensitive to energy and angular momentum transfer through 2nd order



Co-workers

Argonne

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